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SILICON, OXYGEN FREE

Interim Report

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INTRODUCTION

The technical literature reports much data in the absorption of silicon in the 8-12 spectral region. Unfortunately, the various authors did not report on the method of preparing the silicon samples, the source of the silicon and the chemical composition of the samples. There are ample data that show general trends of absorption but only a few papers on quantitative composition of the samples. The following general trends are reported:

- o "oxygen free" silicon has a weak lattice absorption around 9μ.

- o addition of oxygen results in strong absorption at 9μ caused by the oxygen at interstitial sites.

- o the method of crystal growth dramatically affects oxygen content.

- o low concentration oxygen crystals have the same absorption whether single or polycrystalline.

- o some authors have stated without proof that absorption at 9μ is linear with the amount of oxygen present in the crystal.

There are many other trends associated with silicon for non-optical applications. These trends are not reported here.

Methods of Crystal Growth vs Oxygen Content

The technical literature has reported extensively on the methods for growing silicon. These papers reveal that oxygen enters the silicon mainly through the method of growing the crystals. Two widely accepted methods are:

- pulled crystals from a melt using a quartz crucible
- floating zone method

There are variations in these two methods, such as rotating the crystal in the pull method, that contaminate the samples with oxygen. As a reference, the pulled crystals have 10^{18} oxygen atoms/cm^3 while the floating zone crystals have 10^{17} atoms/cm^3. One paper[1] discusses absorption as a function of crystal growth methods. In this paper and others controlled amounts of ^{16}O, ^{17}O and ^{18}O are added so that these isotopes can be used for measurements. They do not significantly alter the overall absorption as seen from an optics application. The isotopes display their own resonances as the temperature is lowered. Also, the strength of the resonances is proportional to the amount of the isotope in the sample. Consider Fig. 1 (their figure 3).
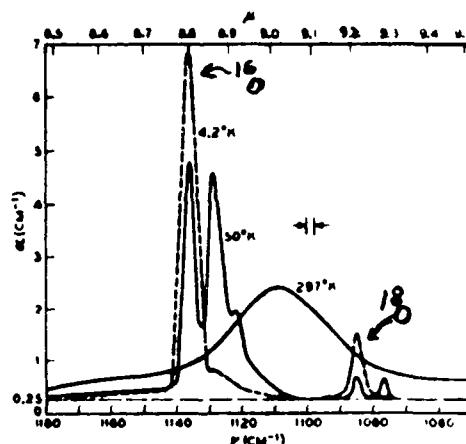

Fig. 3. The absorption coefficient of the 1106 cm^{-1} band at several temperatures for a floating-zone crystal containing oxygen enriched with 13% O^{18} and 1% O^{17}.

1. Hrostowski and Kaiser, Phy Rev Vol 107, No 4, pg. 966

The sample was prepared by replacing 12% of the ^{16}O with ^{18}O. This experiment and others like it showed that the isotopes had their own resonances which were used to prove that the amount of oxygen in the sample was responsible for the strength of the absorption. Additionally, this paper concluded that only one oxygen atom in the form Si_2O, located interstitially, was responsible for the resonances. Unfortunately, this paper gave no quantitative data on the number of oxygen atoms present in the samples.

One paper[2] reports the quantitative content of oxygen in silicon and resulting absorptions. This paper will be discussed in detail. The paper evaluates:

- crystals grown from quartz crucible
- crystals grown from the floating zone technique
- single crystals
- polycrystaline samples

The source of the silion, method of growth, and absorption are given in the paper's Table I.

TABLE I. Absorption coefficient at 9μ of different silicon samples.

Sample No.	Origin and preparation[a]	Absorption coeff at 9 microns	Remarks
104	FM, QC, S	3.2 cm⁻¹	47 ohm cm
13	DP, QC, S	3.6 cm⁻¹	6 ohm cm
08	DP, QC, P	4.5 cm⁻¹	10 ohm cm "densified silicon"
98	FM, FZ, S	1.05 cm⁻¹	70 ohm cm
109	DP, FZ, S	1.05 cm⁻¹	35 ohm cm
06	FM, P	~1.0 cm⁻¹	Microcrystalline, as deposited on the tantalum wire
105	FM, FZ, P	1.05 cm⁻¹	Originally
		1.55 cm⁻¹	FZ in oxygen of 1 mm Hg
85	DP, QC, P	4.2 cm⁻¹	20 ohm cm
		1.3 cm⁻¹	Melted in vacuum
84	DP, QC, P	4.2 cm⁻¹	20 ohm cm
	DP, FZ, P	1.3 cm⁻¹	After several FZ passes, 40 ohm cm

[a] DP = silicon from DuPont (zinc reduction process). FM = silicon from Foote Mineral Company (iodide process). QC = crystallized from quartz crucible. FZ = crystallized by floating zone technique. S = single crystal. P = polycrystalline.

2. Kaiser, Keck, Lange, Phy Rev Vol 101, No 4, pg. 1264

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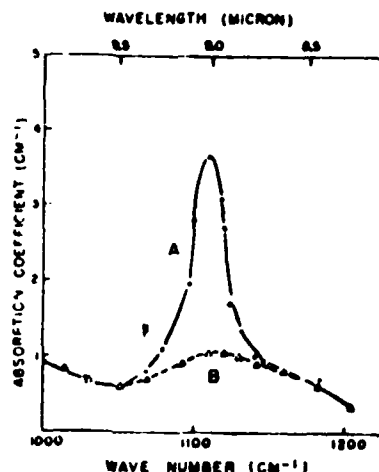Before discussing this table consider the paper's (Fig. 1).

Fig. 2

Fig. 1. Absorption coefficient of silicon at room temperature.
A (sample 13) pulled from a quartz crucible, B (sample 109) pre-
pared by floating zone technique.

This figure shows the dramatic difference between the absorption of a pulled
sample and a sample grown by the floating zone technique. The floating zone
sample (109) is a single crystal. Table I shows that sample (105) is a
polycrystal from the floating zone technique. The absorptions for the single
and polycrystal are the same.

Table I gives some interesting information on possible manufacturing
processes for crystal growth. Sample 85 grown from a quartz crucible gives an
absorption of 4.2 cm^{-1}. However, if the sample is melted in a vacuum to
remove oxygen, the absorption drops to 1.3 cm^{-1}. The point to be made is
that there may be less expensive manufacturing techniques for producing
acceptable samples.

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Table II of the paper gives the concentration of oxygen in the samples:

TABLE II. Comparison between the absorption coefficient at 9μ and the oxygen content of silicon. For history of samples, see Table I.

| Sample No.	Total absorption coefficient at 9μ (cm⁻¹)	Absorption coefficient due to oxygen (cm⁻¹)	Vacuum fusion analysis. Weight percentage of oxygen ×10⁻⁴	Number of O-atoms Vacuum fusion analysis (cm⁻³) ×10¹⁷	Calculated from Eq. (2) (cm⁻³) ×10¹⁷
109	1.05	...	3 ±3	2.7	...
84	1.3	0.3	3 ±3	4.5	0.5
104	3.2	2.2	8 ±3	7.2	3.2
85	4.2	3.2	11 ±3	10.0	4.9

Sample 109 is a single crystal from the floating zone technique. Its total absorption is 1.05 cm^{-1}. The equipment used to measure the absorption was not sensitive enough to measure the absorption due to small amounts of oxygen contamination. At this point it can be assumed that the absorption is due to lattice vibrations. The number of atoms is 2.7×10^{17} atoms/cm^3. Therefore, as a starting point for specifying silicon for optical applications, the following statement is reasonable:

> Silicon for optical lens must contain no more than
> 2.7×10^{17} oxygen atoms/cm^3 or 3×10^{-4} per-
> centage weight of oxygen.

The paper states that absorption measurements at 9 provide a method for quantitative analysis of oxygen in silicon. The limit of detectability is approximately 10^{-5} weight percent oxygen or 10^{16} oxygen atoms per cm^3.

It is interesting to plot the absorptivity as a function of oxygen content:
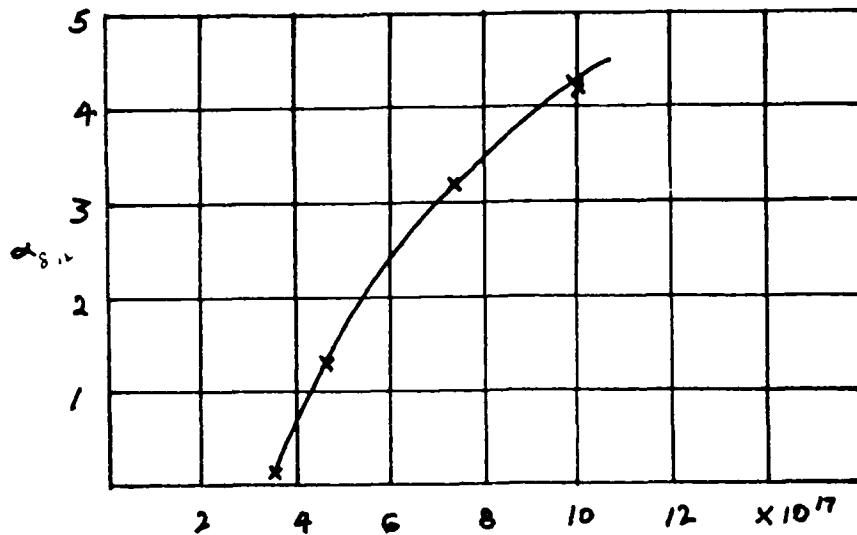
It is clearly shown that oxygen content is the major cause of absorption. Whether or not the function is linear is not important for optical silicon. What is important is that the content not go beyond 2.7×10^{17} atoms/cm^3.

The paper makes an attempt to determine the number of Si - O - Si oscillators in a sample. The theoretical calculations do approximate the experimental data, but not close enough to specify optical material. The theoretical expression is given here just to show what is involved in using an absorption resonance curve to calculate the number of oscillators in the sample.

$$\int \alpha_\nu \, d\nu = N_o \frac{\pi e^2}{3 \mu c} \cdot \frac{(n^2 + 2)^2}{9n}$$

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The following figure shows the absorption results:
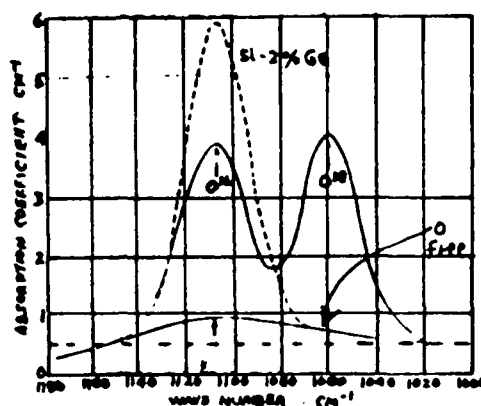
The above data are interesting from the viewpoint that the absorption is considerably below 1 cm^{-1}. Other data (Fig. 2) show a higher α. Both sets of data claim the samples are "oxygen free" or that lattice vibrations dominate the absorption. Yet the silicon with 2% Ge has a smaller absorption coefficient. What is interesting about the 2% Ge samples is that the expected shift of Si - O - Ge molecules from 9μ to 11.1μ was not observed when absorption measurements were made at low temperatures. Apparently the addition of 2% GE simply lowered the absorption coefficient. This leaves some interesting questions unanswered.

1. If 2% addition of Ge lowers the absorption coefficient from 8μ to 12μ, would 4% Ge, 8% Ge . . . 20% Ge lower it even more?

2. Is it possible that a Si lens, mixed with a certain amount of Ge, may be an acceptable lens and may be a substitute for Ge?

3. What is the cost associated with growing silicon with Ge in an oxygen free environment?

4. What are the optical properties of Si-Ge lens?

This integral is approximated with the following result:

$$N_0 = \frac{9n}{(\eta^2 + 2)^2} \cdot \frac{3\mu c}{\pi e^2} \, \alpha_{max} \, H$$

where: α_ν = absorption coef for frequency ν

μ = reduced mass of the oscillator

e = net electronic charge

η = refractive index

α_{max} = absorption coefficient at the band maximum

H = half width of the band

In a qualitative sense, the higher and wider the absorption curve, the greater the number of oscillators.

Silicon Doped with Germanium

It has been established that the lattice vibrations at 9μ dominate the absorption in silicon when the oxygen content is below 10^{17} atoms/cm^3. Is there any way to decrease the lattice contribution? A paper[3] indicates that a small amount of Ge added to the Si decreases the lattice contribution. What happens is the Ge replaces some of the Si atoms in the lattice. The additional mass of the newly formed oscillator (and some other effects) shifts the resonance from 9μ to 11.1μ . Two samples were made with 2% Ge replacing silicon atoms. One sample contained 1.8×10^{18} atoms/cm^3 with 55% ^{18}O, 43.5% ^{16}O, and 1.5% ^{17}O. The other sample was an unsaturated oxygen sample. No details of the content were given.

3. Hrostowski and Alder Jour Chem Phy Vol 33 No 1 pg. 980

Comparison of Silicon and Germanium

Germanium is an accepted material for transmission in the 8 - 12 region. If silicon transmission can equal or approach germanium it too would be accepted. Preliminary data indicate that Si will never be as good as Ge, but it may be acceptable for those applications where the lens thickness is small. Consider published data on the transmission of Ge.

Table 1

Wavelength (micrometers)	Theoretical Max. Trans.	Recommended Minimum Transmission	Recommended Maximum Absorption Coefficient
2.5	46.39 %	45.7 %	0.010 cm^{-1}
3	46.60	45.9	0.010
4	46.80	46.1	0.010
5	46.88	46.2	0.010
6	46.93	46.1	0.012
7	46.96	45.9	0.017
8	46.98	45.7	0.022
9	47.00	45.5	0.025
10	47.00	45.3	0.029
10.6	47.01	45.0	0.035
11	47.01	44.9	0.037
12	47.02	37.6	0.179
13	47.02	38.1	0.169
14	47.03	38.6	0.158

Shown for comparison are theoretical maximum transmissions based on reflection losses only.

The recommended transmission in the 8 - 12 μ region is about 44% for a 1 cm thick sample. If a Si application can approach this transmission it should be acceptable.

The literature gives an expression for transmission as a function of absorption coefficient.

$$t = \frac{16\,n^2 \exp(-\alpha d)}{(n+1)^4 - (n-1)^4 \exp(-2\alpha d)}$$

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where   = transmission coef

           = thickness

           = index of refraction

Using this expression to calculate transmission of Si for n = 3.42, the following table can be used to compare Si to Ge.

Transmission of Si (%)

d(mm) \ α (cm^{-1})	1.0	0.8	0.6	0.4	0.2
3	37	40	43	46	49
5	30	33	36	42	47
10	18	21	27	33	42

It can be seen that for a 3 mm thick sample, an α = 0.8 cm^{-1} is probably good enough. For a 5 mm sample $\alpha \approx 0.5$ cm^{-1} is probably good enough. For a 1 cm thick sample $\alpha \approx 0.3$ cm^{-1} is probably good enough.

Referring to the published data an α for Si, Fig. 2 shows an average $\alpha \approx 0.8$ cm^{-1}. For Si doped with 2% Ge, the average α is close to 0.7 cm^{-1}. Based on the theoretical calculation the following conclusions can be made:

- For 3 mm applications - "oxygen free" Si is acceptable

- For 5 mm applications - Si with 2% Ge is borderline

- For 10 mm applications - Si may not be an acceptable material for high performance systems

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Results

1. The absorption band in Si at 9μ is due to both oxygen contamination and intrinsic lattice vibrations of the Si-O-Si molecule.

2. The oxygen contamination component can be minimized by restricting the oxygen content in a Si sample to 2×10^{17} oxygen atoms/cm^3

- The average value of the absorption coefficient is about

$$0.8 \ cm^{-1}$$

over the 8μ to 12μ region

3. The addition of 2% Ge to a Si sample lowered the intrinsic absorption to about

$$q = 0.7 \ cm^{-1}$$

over the 8μ to 12μ region

Conclusions

1. The absorption in Silicon for the 8μ to 12μ region depends on the amount of oxygen contamination in the sample and on the intrinsic or lattice vibrations of the sample.

2. The oxygen contamination component can be eliminated if the total number of oxygen atoms/cm^3 does not exceed 2×10^{17}

As a starting point specification for optical silicon, the silicon should have no more than 2×10^{17} oxygen atoms per cm^3

3. There is some evidence that controlled amounts of Germanium added to the silicon reduces the intrinsic absorption at 9μ.

4. Si may be substituted for Ge for thin lens applications.

5. Si doped with Ge may be a suitable substitute for Ge for many applications.

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